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(54) **A process for synthesizing phosphonic acid-containing polymers and the polymers thereof.**

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Description

This invention relates generally to a process to synthesize water-soluble phosphonated polymers containing a phosphonate group, and, in addition, which polymers may also contain other functional groups which may be useful when applied to aqueous solutions or environments.

The synthesis of water-soluble phosphonated polymers has generally been limited. This synthesis of vinylic phosphonated polymers containing the phosphonate group has been limited from the point of view that only certain of these kinds of phosphonated monomers are commercially produced.

As a result, the use of these phosphonated water-soluble polymers is extremely limited commercially. It would therefore be an advance in the art if water-soluble polymeric chemical structures could be synthesized on a polymeric backbone which structures would contain the phosphonate group, either in the acid or salt form, and which structures might also contain other functional groups which could enhance the use of these water-soluble phosphonated polymers in certain applications such as dispersants in water treatment, scale inhibitors in natural and industrial waters, flocculants and coagulants, and the like.

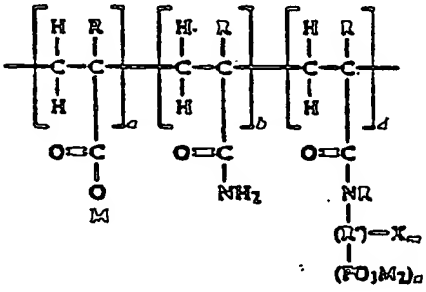
It is desired to develop a synthetic procedure which can generally be applicable to the synthesis of various types of water-soluble polymers containing the phosponate group with or without the additional presence of other functional groups which may be useful when these polymers are added to aqueous systems.

Another aim of this invention is to synthesize and recover certain types of phosphonate containing water-soluble polymers which polymers may contain other functional groups such as hydroxyl, chloro, bromo, iodo, and/or mixtures thereof, which polymers have not heretofore been known or used.

We have discovered a process for modifying water-soluble polymers containing pendant amide functional groups, such polymers primarily derived from acrylamide containing vinylic polymers/copolymers or from alkyl substituted acrylamide containing vinylic polymers or copolymers, and which polymers/copolymers are water soluble and contain pendant amide functional groups derived from acrylamide, methyl acrylamide, ethylacrylamide, and the like.

This process in accordance with the invention uses the equivalent of a transamidation reaction with the pendant amide group on the polymer and a chemical reactant.

The process is to synthesize water-soluble phosphonated polymers having randomly repeated units represented by the general formula



(V)

wherein

R' is a multi-covalent hydrocarbonaceous bridging group having 1 to 16 carbon atoms and being chosen from linear, branched or cyclic alkyl, alkaryl, arylalkyl, aromatic, heterocyclic, olefinic functional groups and mixtures thereof,

X is chosen from Cl, Br, I, -COOM, $-SO_3M$, -OH, -OR,

$$-(-OCH_2-\underset{R}{CH})_pOR$$

and mixtures thereof,

R is individually chosen at each occurrence from H and lower alkyl (C_1-C_4) groups,

M is chosen from hydrogen, lower alkyl (C_1-C_4) groups, alkali metal, an equivalent of alkaline

earth metals, alkylated and tertiary amines, quaternary amines, and ammonium ion, and mixtures thereof, and

a, b and d are integers with the following relationships:
a/b is from zero to 100
b/d is from 0.01 to 100
a/d is from zero to 100,
and the sum of (a+b+d) is sufficient to provide a molecular weight of at least 500, and the ratio of d/(a+b) is from 100:1 to 1:100,

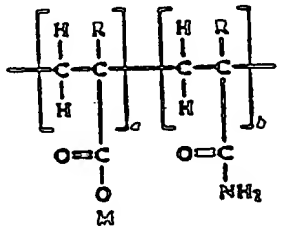
p ranges between 1 and 16,

m ranges between 0 and 16, and

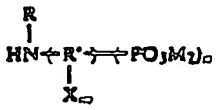
n ranges between 1 and 16, provided that when m is zero, the sum of (m+n) is from 1 to 20,

which process comprises reacting, in a common solvent, at a temperature of at least 100° C

(A) a polymer having a molecular weight of at least 500 and having pendant amide functional groups and being represented by the structure



wherein R, M, a and b have the meaning as above, with (B) a chemical reactant having the structure



(I)

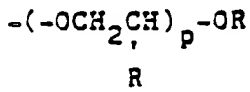
wherein R, R', M, X, p, m and n have the meaning as above,

wherein the mole ratio of chemical reactant to pendant amide groups in the polymer ranges between about 5:1 and about 1:100, and reacting to accomplish at least a 25 percent conversion of chemical reactant to phosphonated pendant groups on the polymer, and then recovering the water-soluble phosphonated polymer.

Preferably

R' has at least two carbon atoms and is linear, cyclic, aromatic and mixtures thereof,

X is chosen from -OH, -COOH,



and mixtures thereof,

R is individually chosen at each occurrence from hydrogen, methyl and ethyl groups,

M is individually chosen at each occurrence from hydrogen, lower alkyl (C_1-C_4) groups, sodium, potassium, tertiary amines, quaternary amines, ammonium and mixtures thereof,

p is from 1 to 12,

m is from 0 to 4,

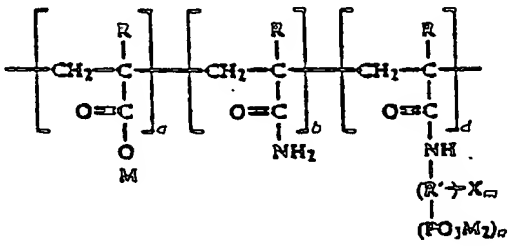
n is from 1 to 4,

and the molecular weight of the water-soluble phosphonated polymer ranges between about 2,000 and about 20,000,000.

The used solvent is preferably chosen from the group consisting of water and water emulsified in a continuous oil phase such that the water-soluble phosphonated polymer is recovered either as a water-in-oil

emulsion or as an aqueous solution.

A preferred embodiment of the invention provides to synthesize water-soluble phosphonated polymers of the formula

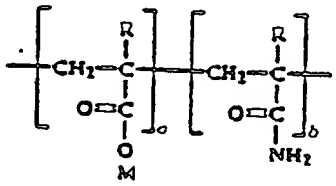


wherein

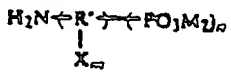
R is H, and

R' is chosen from multi-covalent branched alkyl, linear alkyl or cyclic hydrocarbonaceous bridging groups having 1 to 8 carbon atoms,

which process comprises reacting, in an aqueous solvent (A) a polymer having pendant amide functional groups and represented by the structure



wherein R, M, a and b have the meaning above and the sum of (a + b) achieves a molecular weight of at least 500, with (B) a reactant having the structure



wherein R', M, X, m and n have the meaning above, under the following reaction conditions:

(I) reaction temperature of at least 100° C,

(II) reaction time of at least 1/4 hour,

(III) mole ratio of chemical reactant to polymer ranging between about 2:1 and about 1:50,

(IV) pressure ranging from atmospheric pressure to 35 times atmospheric pressure,

thereby achieving and thereafter recovering said phosphonated polymers.

In said process it is preferred that

R' is a linear alkylene bridging group having 2 to 6 carbon atoms;

X is chosen from -OH, -COOH, $-(-OCH_2CH_2-)_p-OH$ and mixtures thereof;

R is individually chosen at each occurrence from hydrogen and methyl;

M is individually chosen at each occurrence from hydrogen, lower alkyl(C_1-C_4) groups, sodium, potassium, ammonium and mixtures thereof;

a, b and d are integers having the following relationship:

a/b ranges from 0 to 50,

a/d ranges from 0 to 50,

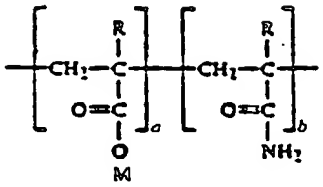
b/d ranges from 0.01 to 10, and

d/(a + b) ranges between 4:1 and 1:20, and

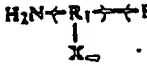
the sum of (a + b + d) is such that the phosphonated polymer has a molecular weight ranging from 1,000 to 20,000,000,

and which process comprises reacting at a temperature of at least 110° C for at least 1/4 hour, in a common

aqueous solvent, (A) a polymer having the structure

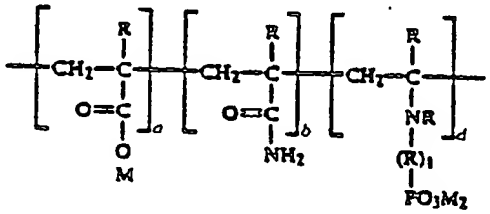


wherein R, M, a and b have the meaning above and the sum of (a + b) is such that the molecular weight of the polymer is at least 2,000, with (B) a chemical reactant having the structure

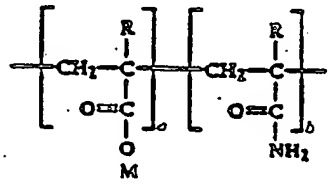


wherein R_1, M and X are defined as above and m is from 0 to 3, n is from 1 to 3 and the sum of (m + n) is from 1 to 4, and the ratio of reactant to polymer ranges between about 1:1 to about 1:10 and the reaction pressure is at least 123 kPa,
and then recovering said phosphonated polymer.

The present invention also provides a phosphonated polymer having the general formula



and being synthesized, in a pressure controlled reactor, by reacting a precursor polymer having the formula



with a chemical reactant

$H_2N\{R_1\}PO_3M_2$

in an aqueous solvent at a temperature of at least 100° C for at least 1/4 hour at a mole ratio of precursor polymer to chemical reactant ranging between about 20:1 to about 1:2, and wherein

- R_1 is a lower linear or branched alkylene bridging group containing from 1 to 6 carbon atoms,
- R is chosen individually at each occurrence from hydrogen and methyl groups,
- M is chosen individually at each occurrence from hydrogen, lower alkyl (C_1-C_4) groups, alkali metal, tertiary amines, quaternary amines and ammonium ions and mixtures thereof,

a, b and d are integers having the relationships:
a/d is from 0 to 100,

a/b is from 0 to 100,
b/d is from 0.01 to 100, and
d/(a + b) ranges between 10:1 and 1:100, and wherein the sum of (a + b + d) is such that the phosphonated polymer has a molecular weight of at least 1,000.

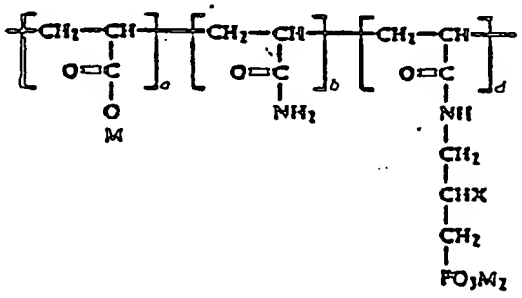
The phosphonated polymer is preferably synthesized in an aqueous reaction solvent at a temperature of at least 120° C for at least 1 hour at a mole ratio of precursor polymer to chemical reactant of from 10:1 to 1:1 and wherein

R is hydrogen,

M is chosen from hydrogen, sodium, potassium and ammonium ions and mixtures thereof,

and the polymer has a molecular weight between 2,000 and 20,000,000.

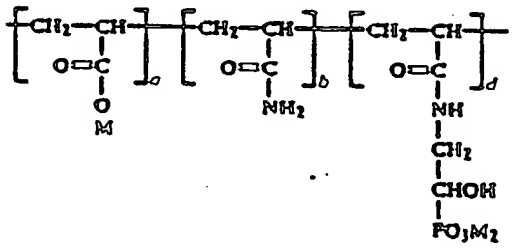
A preferred phosphonated polymer is represented by the general formula



wherein

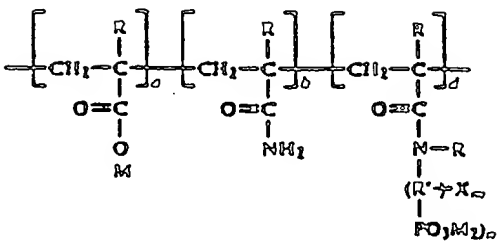
M	is individually chosen at each occurrence from hydrogen, sodium and ammonium ions,
X	is chosen from the group -OH, -COOH, $-(OCH_2CH_2)_p-OH$, $-SO_3H$ and mixtures thereof,
p	is from 1 to 6,
a, b and d	are integers such that
	the sum of (a + b + d) is sufficient to achieve a molecular weight of at least 1,000,
	a/d is from 0 to 100,
	b/d is from 0.01 to 100,
	a/b is from 0 to 100, and
	the ratio d/(a + b) ranges between 5:1 and 1:50.

Another preferred phosphonated polymer is represented by the general formula



wherein M, a, b, d have the above meaning.

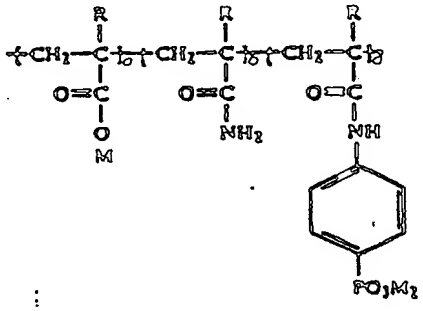
A further phosphonated polymer is represented by the general formula



wherein

R'	is a multivalent hydrocarbonaceous bridging group having 1 to 6 carbon atoms and being chosen from linear alkyl, branched alkyl, cyclic and olefinic groups and mixtures thereof;
X	is chosen from -OH and -COOM and mixtures thereof;
R	is individually chosen at each occurrence from hydrogen and methyl groups;
M	is individually chosen at each occurence from hydrogen, lower (C1-C4) alkyl groups, sodium, potassium and ammonium ions and mixtures thereof;
a, b and d	are integers, the sum of which is such that the molecular weight of the phosphonated polymer is at least 2,000, wherein the following relationship exists: a/b is from 0 to 100, a/d is from 0 to 100, b/d is from 0.01 to 100, and the ratio d/(a + b) is between about 10:1 to about 1:100; m is equal to 0 to 6, n is equal to 1 to 6, and the sum of (m + n) is between 1 and 6.

Another phosphonated polymer is represented by the general formula



wherein

R	is individually chosen at each occurence from hydrogen and methyl groups;
M	is individually chosen at each occurence from hydrogen, a methyl group, sodium, potassium and ammonium ions, and mixtures thereof, and
a, b and d	are the same as above.

THE CHEMICAL REACTANT

The chemical reactant described above is primarily an amino substituted compound which also contains the phosphonate functional group, and wherein the amine functional group contains at least one active hydrogen substituted on the amino nitrogen. Although phosphonate compounds having both primary and secondary amines can react under our transamidation reaction conditions to achieve modified phosphonate containining polymers, it is preferable that when a secondary amine is chosen to accomplish this modification of pendant amide containing polymers, that the alkyl group substituted on the amino nitrogen contain no more than 4 carbon atoms, i.e. the alkyl substitution should be limited to methyl, ethyl, propyl

and butyl functionality, and isomers thereof.

However, it is most preferred that the amine substitution on the phosphonate containing chemical reactant be a primary amino functional group. When a primary amino functional group is used to accomplish the transamidation reaction, the reaction easily proceeds so as to incorporate at least 2, and preferably 60 mole percent of the chemical reactant used into the water-soluble polymer chain containing pendent amide groups.

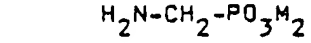
In addition to the amine substitution in the chemical reactant described above, this chemical reactant does contain at least one phosphonate functional group in either its acid form, partial or complete ester form, or its salt form, wherein the salt form is chosen from a salt of an alkali metal, an alkaline earth metal, tertiary amines, quaternary amines, and ammonium ions, and mixtures thereof. The ester or salt forms may be in existence prior to the transamidation reaction or they may be synthesized by known techniques during the transamidation reaction or after the transamidation reaction has been completed.

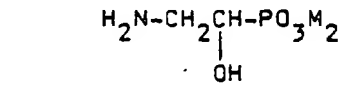
In addition to the phosphonate functional group and the amine functional group, the chemical reactant may also contain other functional groups chosen from the groups consisting of chlorine, bromine, iodine, hydroxyl, ethoxyl, propoxyl, carboxyl, ester, ether, sulfonate groups and the like, and mixtures thereof. Preferably, the chemical reactant is limited to contain a primary amino group responsible for the transamidation reaction, at least one phosphonate group which allows the formation of an anionic phosphonate containing water-soluble polymer, and an hydroxyl, an ethoxylated or propoxylated group or a carboxylate functional group, the presence of which may enhance the activity of water-soluble phosphonate containing polymers synthesized by the process.

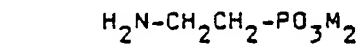
Most preferably, the chemical reactant contains a primary amine, zero or more carboxyl, hydroxyl, or ethoxylated groups, and one or more phosphonate groups either in the free acid form, ester forms, salt form, or mixtures thereof.

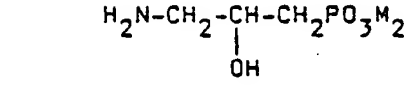
Several preferred species of the chemical reactant described above are demonstrated in the following formulations:

Formula II.

a. 

b. 

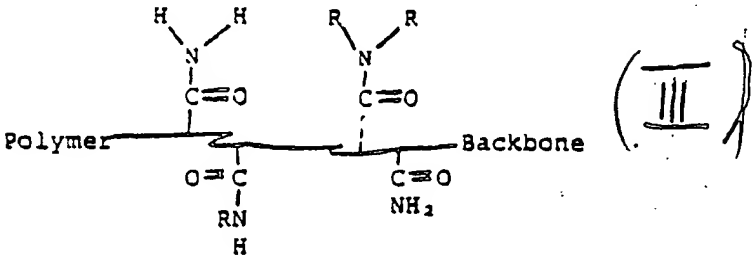
c. 

d. 

wherein, M is chosen from H, lower alkyl (C_1-C_4) groups, alkali metals, an equivalent amount of alkaline earth metals, and alkylated amine, ammonium, or quaternary nitrogen containing moieties.

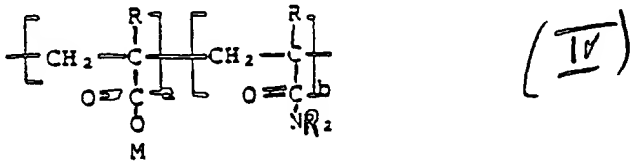
THE PENDANT ACRYLAMIDE CONTAINING POLYMERS

The pendant acrylamide containing polymers are water-solube polymers which have a general structure allowing the presence of a pendant amide group as demonstrated in Formula III:



In Formula III, as one can observe, the pendant amide group may be a primary amide, a secondary amide, or a tertiary amide group and mixtures thereof. Preferably, to obtain reasonable conversions of these pendant amide groups to the phosphonate containing functional groups described above, the pendant amide group is a primary amide group.

The most likely water-soluble polymers containing pendant amide functionality which polymers are easily modified under the conditions of our transamidation reaction, are those water-soluble polymers described by Formula IV:



In Formula IV,

R is independently chosen, at each occurrence, from the group consisting of hydrogen, and lower alkyl groups containing from 1-4 carbon atoms;

M is independently chosen, at each occurrence, from hydrogen, lower alkyl (C_1-C_4) groups, alkali metals, an equivalent amount of alkaline earth metals and ammonium ions and mixtures thereof;

and a and b are integers having the following relationships:

a/b ranges between 0 to 100, and

a + b is sufficient so as to provide a polymer having a molecular weight of at least 500. Preferably the sum a + b is sufficient to provide a molecular weight ranging between about 1,000-20,000,000.

As can be seen, the polymers described above may be homopolymers of acrylamide or its alkyl homologs, i.e. methacrylamide and the like, they may be copolymers of acrylamide with acrylic acid or its lower alkyl (C_1-C_4) esters, and their homologs such as methacrylic acid or methylacrylate and the like, or they may be terpolymers and above with other monomers of a vinylic nature which terpolymers contain acrylamide and acrylic acid or its esters, and their homologs such as methacrylic acid, methyl acrylate, metharcylamide, and the like.

THE CHEMICAL REACTION

The chemical reaction which is preferred to obtain the phosphonate polymers of this invention is a reaction which can generally be referred to as a transamidation reaction. This reaction substitutes an amine compound which may also contain other functional groups such as the phosphonate function group for the nitrogen portion of a pendant amide group contained on a polymeric backbone as described above. This transamidation reaction has been discovered to be a general reaction which can achieve the substitution of the amine and phosphonate containing moiety for the amide nitrogen group of the pendant amide functionality of a water-soluble polymer, thereby obtaining unique phosphonated polymers.

The reaction conditions require that polymers containing pendant amide groups be dissolved or readily dispersed in a solvent which is a common solvent for the chemical reactant of the class described above. In

other words, both the polymer which is to be modified and the chemical reactant should be soluble or dispersible in the same solvent system.

Common solvents which have been found useful in this reaction include, but are not limited to, water, diethylenglycol dimethylether, dimethylformamide, dimethylsulfoxide, admixtures thereof, and admixtures of these solvents, either singly or taken together with other miscible solvents such as ethanol, tertiary butanol diglyme, and the like.

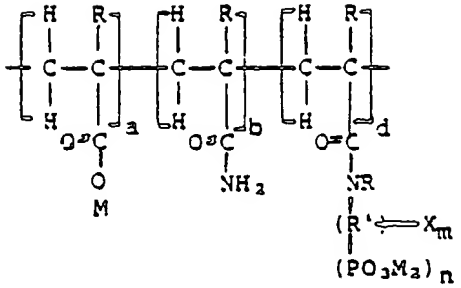
A preferred solvent which is a common solvent for both the polymer containing pendant amide groups and the chemical reactants above is water, particularly if the polymer containing pendant amide group is initially water-soluble, as in the case of most acrylamide containing vinylic polymers. Another preferred common solvent for our reaction is a water-in-oil emulsion wherein the dispersed water phase contains dissolved therein both the polymers containing pendant amide groups and the chemical reactants described above.

After having dissolved the polymers containing pendant amide groups in the common solvent, preferably water, the chemical reactant can be added to obtain a solution or dispersion of amide containing polymer and the chemical reactants of this invention. Whether the polymer or the reactant is first added to the common solvent is of no consequence. This admixture is then added to or contained in a reaction vessel capable of withstanding a pressurized chemical reaction, for example, a Parr Bomb type of vessel. The vessel is closed and then heated to a temperature of at least 100°C, preferably at least 110°C, and most preferably to a temperature of at least 120°C. If the temperature is increased above 100°C, the vessel contents can expand and the pressure within the vessel can exceed one atmosphere and depending upon the solvent, the phosphonates used or the reactants used, can reach up to about 5 to 15 atmospheres, and possibly more. The pressure within the reaction vessel is a non-controlled variable and is controlled only to the extent that the vessel is closed, that a reaction temperature of at least 100°C or higher is reached, and the vessel may contain solvents or reactants of more or less volatile nature, which solvents and reactants have vapor pressures of such a nature that pressure vessels are required at temperatures above 100°C.

Once the reaction vessel contents have reached at least 100°C, and preferably 110°C, the reaction is allowed to occur for at least 3 minutes at this temperature, and preferably for whatever length of time is necessary to accomplish a minimum of at least a 2 percent, and preferably at least a 25 percent, conversion of the added amount of chemical reactant. The chemical reactant is, of course, converted to a pendant phosphonate containing substituted amide being the product of the transamidation chemical reaction summarized above. If the polymer is a homopolymer of acrylamide, methacrylamide, or a copolymer of vinyl amide containing monomers such that no other pendant functional group is present besides amide functional groups, the condition of the reaction is such that at least some degree of amide hydrolysis may also occur in those reactions in which water or a water containing solvent is utilized. In such cases, a carboxylate functional group is also obtained in addition to the phosphonate modified amide and any unreacted starting amide groups from the starting polymer.

Polymer recovery may be accomplished in several ways known to the person familiar with the art. For example, the polymers may be precipitated by addition of precipitating solvents, or non-solvents, to the reaction mixture. For example, methanol or acetone may be added to the reaction mixture either as is or after concentration by distillation or vacuum distillation to precipitate the polymers. The polymers may also be recovered by vacuum distillation of solvent and unreacted chemical reactant from the reaction product mixture. The polymers may also be recovered by gel permeation chromatographic techniques, however, for the most part the polymers are recovered simply as a solution in the solvent used to perform the transamidation reaction, and used as such.

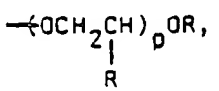
Preferably, the process is a method to synthesize water-soluble phosphonated polymers having randomly repeated mer units represented by the formula:



wherein

R' is a multi-covalent hydrocarbonaceous bridging group having from one to sixteen carbon atoms and being chosen from linear alkyl, branched alkyl, cyclic, aromatic, heterocyclic, and mixtures thereof, functional groups;

X is chosen from -COOM, OR,



and mixtures thereof;

R is individually chosen at each occurrence from H and lower alkyl (C_1-C_4) groups;

M is chosen from hydrogren, lower alkyl (C_1-C_4) groups, alkali metal, 1/2 alkaline earth metal, tertiary amines, quaternary amines, and ammonium ions and mixtures thereof;

and wherein

a, b, and d are integers with the following relationships;

a/b is from zero to 100,

b/d is from 0.01 to 100,

a/d is from zero to 100,

and the sum of a + b + d is sufficient to provide a molecular weight of at least 3,000,

and the ratio of d:(a + b) is from 20:1 to 1:100;

and wherein

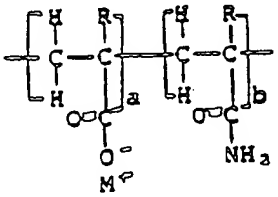
p ranges from 1 and 16,

m ranges between 0 and 16,

n ranges between 1 and 16, provided that when m is zero, the sum of m + n is from 1 to 20;

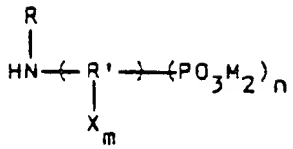
which process comprises reacting, in a common solvent, at a temperature of at least 100° C:

A. a polymer having a molecular weight of at least 500, and having pendant amide functional groups, and represented by the structure:



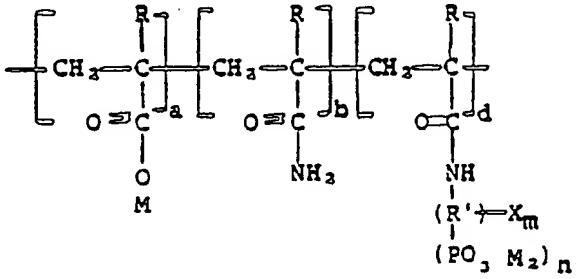
wherein R, M, a, b have the same meanings as above; with

B.a chemical reactant having the structure:



wherein R, R', M, X, p, m, and n have the meanings above; and wherein the mole ratio of chemical reactant to pendant amide groups ranges between about 5:1 to about 1:100; and wherein the reaction occurs for an effective amount of time to accomplish at least a 25-60 percent conversion of chemical reactant to water-soluble phosphonated polymer; and then recovering the water-soluble phosphonated polymer.

Most preferably, our process is a method for the synthesis of water-soluble phosphonted polymers represented by the formula:



wherein

R' is chosen from multi-covalent, branched alkyl, linear alkyl or cyclic hydrocarbonaceous bridging groups having from one to eight carbon atoms;

X is chosen from -COOM, $(OCH_2CH_2)OR$, OH, and mixtures thereof;

R is individually chosen at each occurrence from hydrogen and C_1 to C_4 lower alkyl groups;

M is individually chosen at each occurrence from hydrogen, lower alkyl (C_1-C_4) groups, alkali metals, and ammonium ions,

m ranges between 0 to 6;

n ranges between 1 to 4;

a, b, and d are integers with the following relationships:

a/b ranges from 0 to 100,

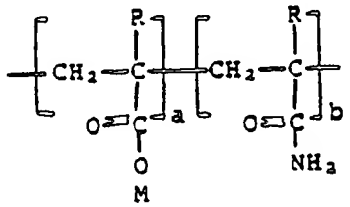
a/d ranges from 0 to 100,

b/d ranges from 0.01 to 100, and

the ratio d:(a+b) is between about 5:1 to about 1:25, and

wherein the occurrence of mer units of a, b, and d is random and the sum of a+b+d will achieve a molecular weight of at least 1000; which process comprises reacting, in an aqueous solvent:

A. a polymer having pendant amide functional groups and represented by the structure:

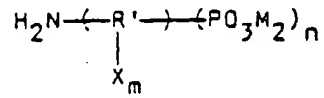


wherein

R, M, a, and b have the meanings above and wherein the sum of a+b achieves a molecular weight of at

least 500; and

B. a chemical reactant having the structure:



wherein R', M, X, m, and n have the meanings above;

under the following reaction conditions:

I. a reaction temperature of at least 100 °C and preferably at least 110 °C;

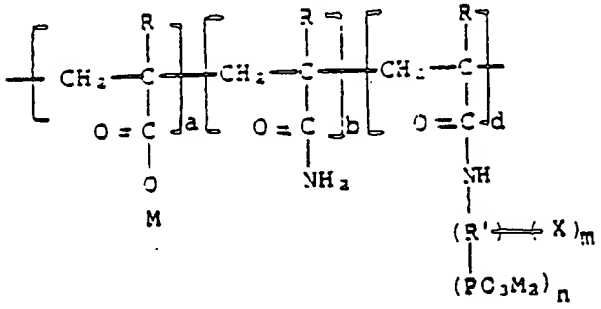
II. a reaction time of at least 1/4 hour and preferably at least 1/2 hour;

III. a mole ratio of chemical reactant to polymer ranging between about 2:1 to about 1:50;

IV. a pressure ranging from atmospheric pressure to 35 times atmospheric pressure, or more;

thereby achieving the synthesis of the phosphonated polymers described above.

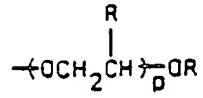
It is particularly of interest that our synthetic procedures permit the synthesis of a phosphonated polymer represented by:



wherein:

R' is a linear or branched alkylene bridging group having from 1 to 6 carbon atoms;

X is chosen from -OH, -COOM, and



and mixtures thereof;

R is individually chosen, at each occurrence, from the group hydrogen, methyl and ethyl groups;

M is individually chosen, at each occurrence, from the group hydrogen, lower alkyl (C_1-C_4) groups, sodium, potassium, ammonium ions and mixtures thereof;

p is from 1 to 12;

m is from 0 to 3;

n is from 1 to 3; and

a, b, and d are integers having the relationships:

a/d is from 0 to 50,

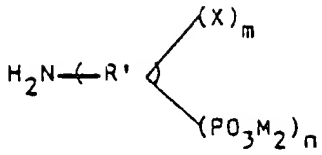
a/b is from 0 to 50,

b/d is from 0.1 to 20,

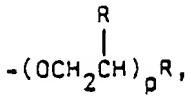
d:(a + b) is from 5:1 to 1:10,

the sum of a + b + d is sufficient to provide a molecular weight of at least 1,000; which process comprises the reaction, in an aqueous solvent, for at least 1/4 hour at a temperature of at least 110 °C, in a pressure controlling reactor, of the ingredients:

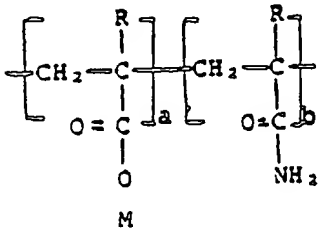
A. a reactant:



wherein X is from the group -OH, -COOM,



and mixtures thereof, and
wherein R', M, p, m and n have the above meanings; and
B. a water-soluble vinyl polymer having pendant amide groups represented by:



wherein R, M, a, and b have the above meanings; and wherein the mole ratio of reactant to pendant amide groups ranges between about 1:1 to about 1:5;
and then recovering the phosphonated polymer.

To further illustrate our invention, we provide the following examples.

Example I

A solution of poly(acrylic acid [25 mole %]: acrylamide [75 mole%]) (27.5% actives, 37.2g), 3-aminopropyl phosphonic acid (4g), sodium hydroxide (50% solution, 2.3g.) was heated to 150°C for five hours. The product was characterized by L.C. and C13, P31 NMR methods. The molecular weight of the polymer was found to be 11,100. NMR analysis of the sample showed that the polymer contained 8 mole % N-3-phosphonopropyl acrylamide.

In addition, the following polymers are synthesized if acrylamide containing polymers were reacted according to the procedures described above with the following chemical reactants. The obtained polymer products are described in Table I.

TABLE I

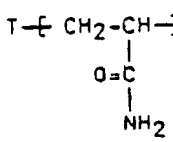
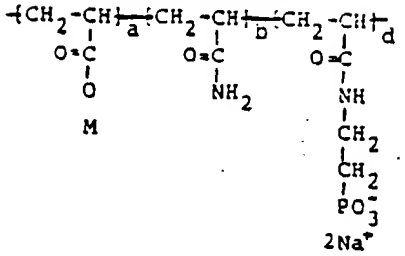
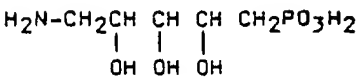
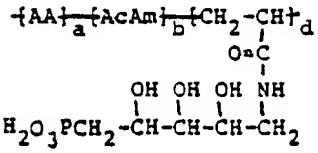
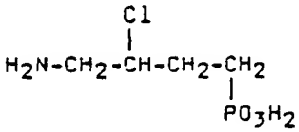
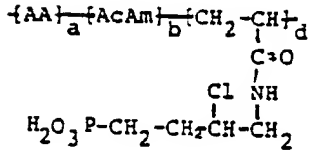
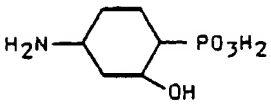
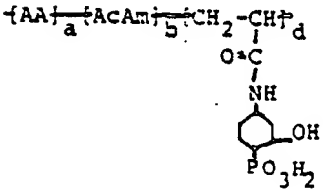
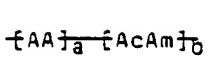
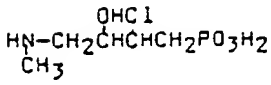
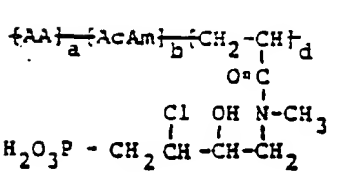
Starting Polymer	Starting Chemical Reactant	Product Polymer
 T = any terminal group	$H_2N-CH_2CH_2PO_3Na_2$	
"		
"		
"		
		

TABLE I
(Continued)

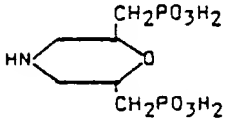
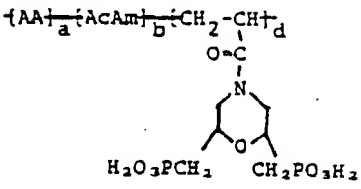
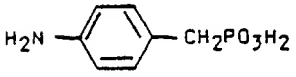
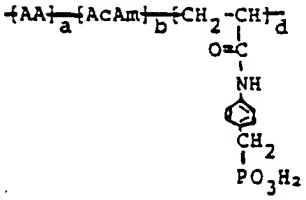
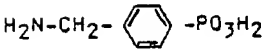
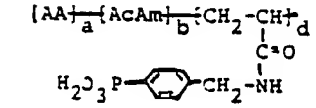
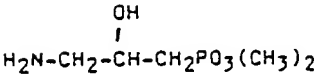
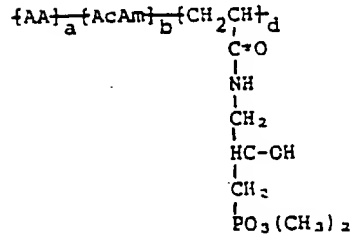
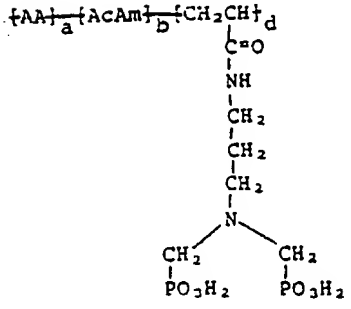
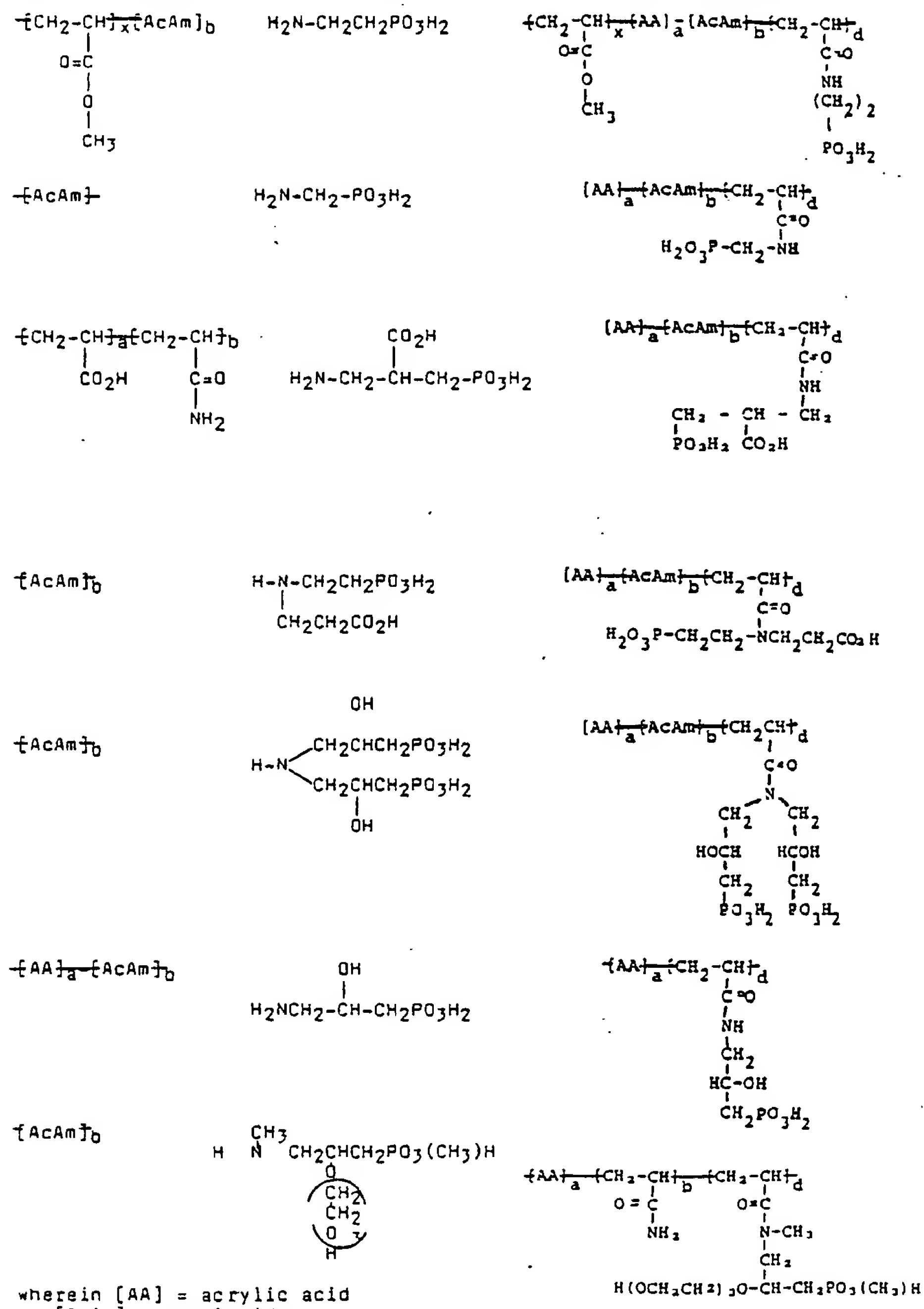
Starting Polymer	Starting Chemical Reactant	Product Polymer
$\{AA\}_a\{AcAm\}_b$		
$\{AcAm\}_b$		
$\{AcAm\}_b$		
$\{AcAm\}_b$		
$\{AcAm\}_b$	$H_2N-CH_2-CH_2-CH_2N(CH_2PO_3H_2)_2$	

TABLE I
(Continued)

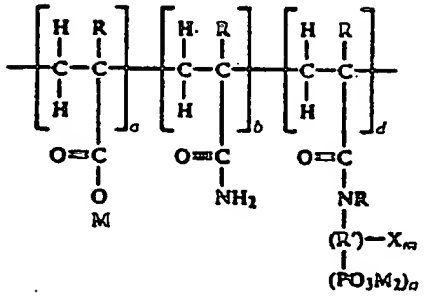
Starting Polymer	Starting Chemical Reactant	Product Polymer



wherein [AA] = acrylic acid
[AcAm] = acrylamide
a, b, d, R, M, have meanings as described above

Claims

1. A process to synthesize water-soluble phosphonated polymers having randomly repeated units represented by the general formula

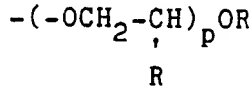


(V)

wherein

R' is a multi-covalent hydrocarbonaceous bridging group having 1 to 16 carbon atoms and being chosen from linear, branched or cyclic alkyl, alkaryl, arylalkyl, aromatic, heterocyclic, olefinic functional groups and mixtures thereof,

X is chosen from Cl, Br, I, -COOM, $-SO_3M$, -OH, -OR,



and mixtures thereof,

R is individually chosen at each occurrence from H and lower alkyl (C_1-C_4) groups,

M is chosen from hydrogen, lower alkyl (C_1-C_4) groups, alkali metal, an equivalent of alkaline earth metals, alkylated and tertiary amines, quaternary amines, and ammonium ion, and mixtures thereof, and

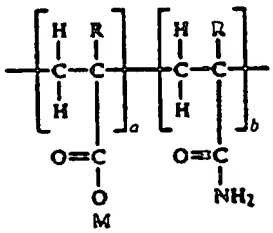
a, b and d are integers with the following relationships:
a/b is from zero to 100
b/d is from 0.01 to 100
a/d is from zero to 100,
and the sum of (a+b+d) is sufficient to provide a molecular weight of at least 500, and the ratio of d/(a+b) is from 100:1 to 1:100,

p ranges between 1 and 16,

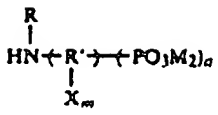
m ranges between 0 and 16, and

n ranges between 1 and 16, provided that when m is zero, the sum of (m+n) is from 1 to 20,

which process comprises reacting, in a common solvent, at a temperature of at least 100° C
(A) a polymer having a molecular weight of at least 500 and having pendant amide functional groups and being represented by the structure



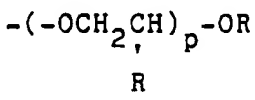
wherein R, M, a and b have the meaning as above, with (B) a chemical reactant having the structure



(I)

wherein R, R', M, X, p, m and n have the meaning as above,
wherein the mole ratio of chemical reactant to pendant amide groups in the polymer ranges between about 5:1 and about 1:100, and reacting to accomplish at least a 25 percent conversion of chemical reactant to phosphonated pendant groups on the polymer, and then recovering the water-soluble phosphonated polymer.

2. The process of claim 1 wherein
   R' has at least two carbon atoms and is linear, cyclic, aromatic and mixtures thereof,
   X is chosen from -OH, -COOH,

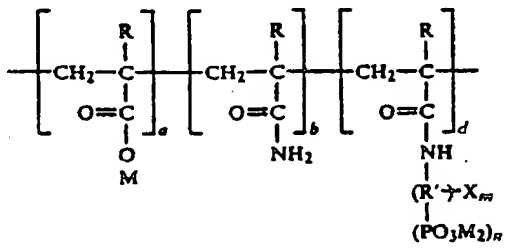


   and mixtures thereof,
   R is individually chosen at each occurrence from hydrogen, methyl and ethyl groups,
   M is individually chosen at each occurrence from hydrogen, lower alkyl (C_1-C_4) groups, sodium, potassium, tertiary amines, quaternary amines, ammonium and mixtures thereof,
   p is from 1 to 12,
   m is from 0 to 4,
   n is from 1 to 4,
   and the molecular weight of the water-soluble phosphonated polymer ranges between about 2,000 and about 20,000,000.

3. The process of claim 1 or 2 wherein the common solvent is chosen from the group consisting of water, dimethylformamide, dimethylsulfoxide, diethyleneglycol dimethylether and mixtures thereof.

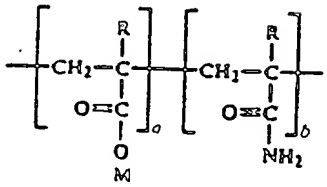
4. The process of claim 1 or 2 wherein the solvent is chosen from the group consisting of water and water emulsified in a continuous oil phase such that the water-soluble phosphonated polymer is recovered either as a water-in-oil emulsion or as an aqueous solution.

5. The process of any of claims 1 to 4 to synthesize water-soluble phosphonated polymers of formula V

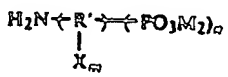


wherein
   R is H, and
   R' is chosen from multi-covalent branched alkyl, linear alkyl or cyclic hydrocarbonaceous bridging groups having 1 to 8 carbon atoms,
which process comprises reacting, in an aqueous solvent (A) a polymer having pendant amide

functional groups and represented by the structure



wherein R, M, a and b have the meaning above and the sum of (a + b) achieves a molecular weight of at least 500, with (B) a reactant having the structure



wherein R', M, X, m and n have the meaning above, under the following reaction conditions:

(I) reaction temperature of at least 100° C,

(II) reaction time of at least 1/4 hour,

(III) mole ratio of chemical reactant to polymer ranging between about 2:1 and about 1:50,

(IV) pressure ranging from atmospheric pressure to 35 times atmospheric pressure,

thereby achieving and thereafter recovering said phosphonated polymers.

6. The process of claim 5 wherein

R' is a linear alkylene bridging group having 2 to 6 carbon atoms;

X is chosen from -OH, -COOH, -(-OCH_2CH_2-)$_p$-OH and mixtures thereof;

R is individually chosen at each occurrence from hydrogen and methyl;

M is individually chosen at each occurrence from hydrogen, lower alkyl(C_1-C_4) groups, sodium, potassium, ammonium and mixtures thereof;

a, b and d are integers having the following relationship:

a/b ranges from 0 to 50,

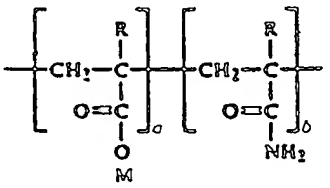
a/d ranges from 0 to 50,

b/d ranges from 0.01 to 10, and

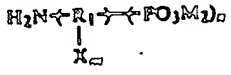
d/(a + b) ranges between 4:1 and 1:20, and

the sum of (a + b + d) is such that the phosphonated polymer has a molecular weight ranging from 1,000 to 20,000,000,

and which process comprises reacting at a temperature of at least 110° C for at least 1/4 hour, in a common aqueous solvent, (A) a polymer having the structure



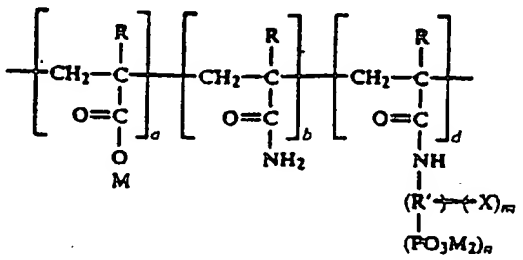
wherein R, M, a and b have the meaning above and the sum of (a + b) is such that the molecular weight of the polymer is at least 2,000, with (B) a chemical reactant having the structure



wherein R_1, M and X are defined as above and m is from 0 to 3, n is from 1 to 3 and the sum of (m + n) is from 1 to 4, and the ratio of reactant to polymer ranges between about 1:1 to about 1:10 and the reaction pressure is at least 123 kPa,
and then recovering said phosphonated polymer.

7. The process of claim 5 or 6 wherein the solvent is water or a water-in-oil emulsion.

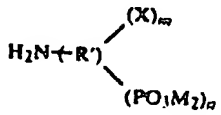
8. The process of claim 1 or 2 to synthesize a phosphonated polymer of formula V



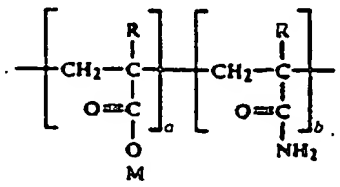
wherein

R'	is a linear or branched alkylene bridging group having 1 to 6 carbon atoms,
X	is chosen from -OH and -COOH and mixtures thereof,
R	is individually chosen at each occurrence from hydrogen, methyl and ethyl groups,
M	is individually chosen at each occurrence from hydrogen, lower alkyl (C_1-C_4) groups, sodium, potassium, tertiary amines, quaternary amines and ammonium ions and mixtures thereof;
m	is from 0 to 3,
n	is from 1 to 3, and
	the sum of (n + m) is from 1 to 4,
a, b and d	are integers having the relationships:
	a/d is from 0 to 50,
	a/b is from 0 to 50,
	b/d is from 0.1 to 20,
	d/(a + b) is from 5:1 to 1:10,
	the sum of (a + b + d) is sufficient to provide a molecular weight of at least 2,000,

which process comprises reacting in an aqueous solvent, for at least 1/2 hour at a temperature of at least 110° C, in a pressure controlled reactor the ingredients
(A) a chemical reactant of the formula

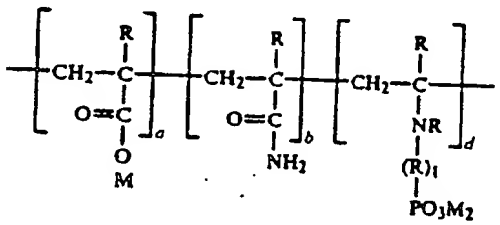


wherein R', X, M, m and n have the above meaning, and
(B) a water-soluble vinyl polymer having pendant amide groups represented by the formula

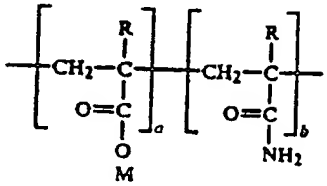


wherein R, M, a and b have the above meaning, and wherein the mole ratio of reactant to pendant amide groups on the polymer ranges between about 1:1 to about 1:5,
and then recovering the phosphonated polymer.

9. A phosphonated polymer having the general formula



and being synthesized, in a pressure controlled reactor, by reacting a precursor polymer having the formula



with a chemical reactant

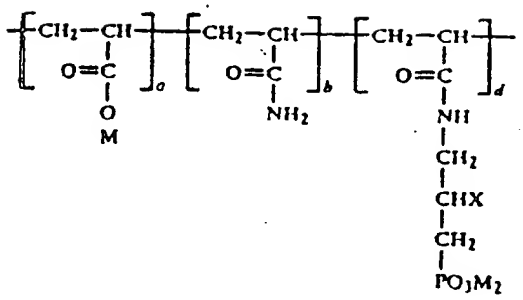
$H_2N\{R_1\}PO_3M_2$

in an aqueous solvent at a temperature of at least 100° C for at least 1/4 hour at a mole ratio of precursor polymer to chemical reactant ranging between about 20:1 to about 1:2, and wherein

R_1 is a lower linear or branched alkylene bridging group containing from 1 to 6 carbon atoms,
R is chosen individually at each occurrence from hydrogen and methyl groups,
M is chosen individually at each occurrence from hydrogen, lower alkyl (C_1-C_4) groups, alkali metal, tertiary amines, quaternary amines and ammonium ions and mixtures thereof,
a, b and d are integers having the relationships:
a/d is from 0 to 100,
a/b is from 0 to 100,
b/d is from 0.01 to 100, and
d/(a+b) ranges between 10:1 and 1:100, and wherein the sum of (a+b+d) is such that the phosphonated polymer has a molecular weight of at least 1,000.

10. The phosphonated polymer of claim 9 which is synthesized in an aqueous reaction solvent at a temperature of at least 120° C for at least 1 hour at a mole ratio of precursor polymer to chemical reactant of from 10:1 to 1:1 and wherein
R is hydrogen,
M is chosen from hydrogen, sodium, potassium and ammonium ions and mixtures thereof,
and the polymer has a molecular weight between 2,000 and 20,000,000.

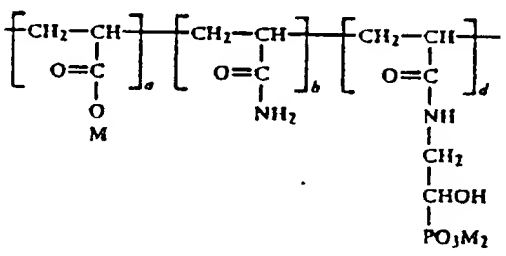
11. The phosphonated polymer represented by the general formula



wherein

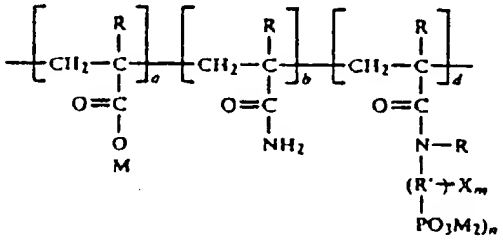
M	is individually chosen at each occurrence from hydrogen, sodium and ammonium ions,
X	is chosen from the group -OH, -COOH, $-(OCH_2CH_2)_p$-OH, $-SO_3H$ and mixtures thereof,
p	is from 1 to 6,
a, b and d	are integers such that the sum of (a + b + d) is sufficient to achieve a molecular weight of at least 1,000, a/d is from 0 to 100, b/d is from 0.01 to 100, a/b is from 0 to 100, and the ratio d/(a + b) ranges between 5:1 and 1:50.

12. The phosphonated polymer represented by the general formula



wherein M, a, b, d have the meaning as defined in claim 11.

13. The phosphonated polymer represented by the general formula



wherein

R'	is a multivalent hydrocarbonaceous bridging group having 1 to 6 carbon atoms and being chosen from linear alkyl, branched alkyl, cyclic and olefinic groups and

mixtures thereof;

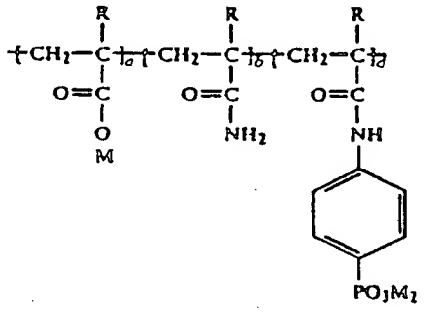
X — is chosen from -OH and -COOM and mixtures thereof;

R — is individually chosen at each occurrence from hydrogen and methyl groups;

M — is individually chosen at each occurence from hydrogen, lower (C1-C4) alkyl groups, sodium, potassium and ammonium ions and mixtures thereof;

a, b and d — are integers, the sum of which is such that the molecular weight of the phosphonated polymer is at least 2,000,
wherein the following relationship exists:
a/b is from 0 to 100,
a/d is from 0 to 100,
b/d is from 0.01 to 100, and
the ratio d/(a + b) is between about 10:1 to about 1:100;
m is equal to 0 to 6,
n is equal to 1 to 6, and
the sum of (m + n) is between 1 and 6.

14. The phosphonated polymer represented by the general formula



wherein

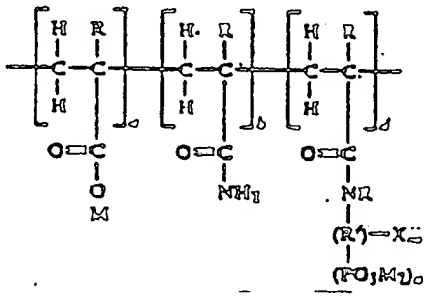
R — is individually chosen at each occurence from hydrogen and methyl groups;

M — is individually chosen at each occurence from hydrogen, a methyl group, sodium, potassium and ammonium ions, and mixtures thereof, and

a, b and d — are the same as in claim 13.

Revendications

1. Procédé pour synthétiser des polymères phosphonés solubles dans l'eau ayant des motifs qui se répètent de façon aléatoire, représentés par la formule générale



(V)

dans laquelle

R' — est un groupe de pontage hydrocarboné multi-covalent ayant de 1 à 16 atomes de carbone ce groupe étant choisi parmi les groupes fonctionnels linéaires, ramifiés ou cycliques alkyles, alkaryles, arylalkyles, aromatiques, hétérocycliques, oléfiniques, et

leurs mélanges,

X est choisi parmi Cl, Br, I, -COOM, $-SO_3M$, -OH, -OR,

$$-(-OCH_2-\underset{R}{CH})_pOR$$

et leurs mélanges,

R est choisi de façon individuelle, à chaque cas, parmi H et les groupes alkyles inférieurs en C_1-C_4,

M est choisi parmi l'hydrogène, les groupes alkyles inférieurs en C_1-C_4, un métal alcalin, un équivalent de métaux alcalino-terreux, les amines alkylées et tertiaires, les amines quaternaires, ainsi que l'ion ammonium, et leurs mélanges, et

a, b et d sont des nombres entiers avec les relations suivantes :
a/b va de zéro à 100
b/d va de 0,01 à 100
a/d va de zéro à 100
et la somme de (a + b + d) est suffisante pour donner un poids moléculaire d'au moins 500, et le rapport d/(a + b) va de 100:1 à 1:100,

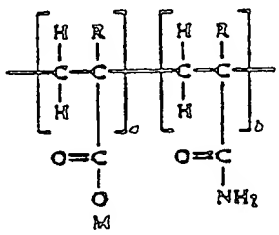
p varie entre 1 et 16,

m varie entre 0 et 16, et

n varie entre 1 et 16, à la condition que lorsque m est zéro, la somme de (m + n) va de 1 à 20,

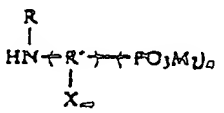
ledit procédé comportant la mise en réaction, dans un solvant commun, à une température d'au moins 100 °C, de

(A) un polymère ayant un poids moléculaire d'au moins 500 et comportant des groupes fonctionnels amides pendants, et étant représenté par la structure



dans laquelle R, M, a et b ont la signification donnée plus haut,

avec (B) un réactif chimique ayant la structure



(I)

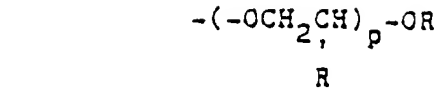
dans laquelle R, R', M, X, p, m et n ont la signification donnée plus haut,

de telle sorte que le rapport molaire entre le réactif chimique et les groupes amides pendants dans le polymère soit compris entre environ 5:1 et environ 1:100, et la réaction étant effectuée de façon à obtenir au moins une transformation à 25% du réactif chimique pour obtenir des groupes phosphonés pendants sur le polymère, et ledit procédé comportant ensuite la récupération du polymère phosphoné soluble dans l'eau.

2. Procédé selon la revendication 1 dans lequel

R' a au moins deux atomes de carbone et est linéaire, cyclique, aromatique, ainsi que les mélanges de celui-ci,

X est choisi parmi -OH, -COOH,



et leurs mélanges,

R est choisi de façon individuelle à chaque fois parmi l'hydrogène, et les groupes méthyle et éthyle,

M est choisi, de façon individuelle, à chaque fois parmi l'hydrogène, les groupes alkyles inférieurs en C_1-C_4, le sodium, le potassium, les amines tertiaires, les amines quaternaires, l'ammonium et leurs mélanges,

p va de 1 à 12,

m va de 0 à 4,

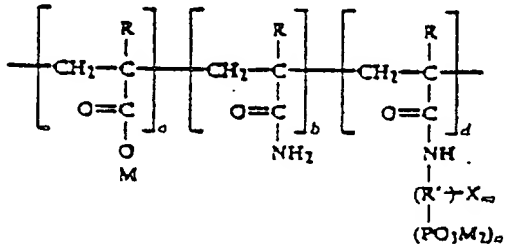
n va de 1 à 4,

et le poids moléculaire du polymère phosphoné soluble dans l'eau s'étend entre environ 2000 et environ 20 000 000.

3. Procédé selon la revendication 1 ou 2, dans lequel le solvant commun est choisi parmi le groupe constitué par l'eau, le diméthylformamide, le diméthylsulfoxyde, l'éther diméthylique du diéthylèneglycol, et leurs mélanges.

4. Procédé selon la revendication 1 ou 2, dans lequel le solvant est choisi parmi le groupe constitué par l'eau et l'eau émulsifiée dans une phase huileuse continue, de façon que le polymère phosphoné soluble dans l'eau soit récupéré sous forme d'une émulsion eau dans l'huile ou sous forme d'une solution aqueuse.

5. Procédé selon l'une quelconque des revendications 1 à 4, pour synthétiser les polymères phosphonés solubles dans l'eau de formule V

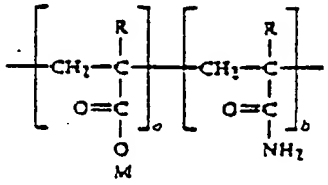


dans laquelle

R est H, et

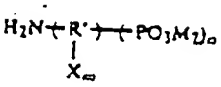
R' est choisi parmi les groupes de pontage hydrocarbonés multi-covalents, ayant de 1 à 8 atomes de carbone, d'alkyles ramifiés, d'alkyles linéaires ou de cycles,

ledit procédé comportant la mise en réaction, dans un solvant aqueux (A) d'un polymère ayant des groupes fonctionnels amides pendants, et représenté par la structure



dans laquelle R, M, a et b ont la signification donnée plus haut et la somme de (a+b) conduit à un

poids moléculaire d'au moins 500,
avec (B) un réactif ayant la structure



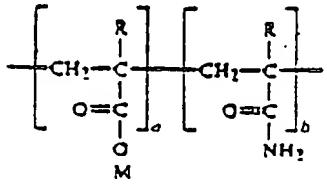
dans laquelle R', M, X, m et n ont la signification donnée plus haut, sous les conditions suivantes de réaction :

(I) température de réaction d'au moins 100 °C,
(II) temps de réaction d'au moins 1/4 heure,
(III) rapport molaire du réactif chimique au polymère s'étendant entre environ 2:1 et environ 1:50,
(IV) pression allant de la pression atmosphérique à 35 fois la pression atmosphérique,

de façon à obtenir et à récupérer ensuite lesdits polymères phosphonés.

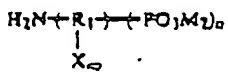
6. Procédé selon la revendication 5 dans lequel
R' est un groupe alkylène linéaire de pontage ayant de 2 à 6 atomes de carbone;
X est choisi parmi -OH, -COOH, -(-OCH_2CH_2-)$_p$-OH et leurs mélanges;
R est choisi de façon individuelle à chaque fois à partir de l'hydrogène et du méthyle;
M est choisi individuellement à chaque fois à partir de l'hydrogène, des groupes alkyles inférieurs en C_1-C_4,du sodium, du potassium, de l'ammonium et de leurs mélanges;
a, b et d sont des nombres entiers ayant la relation suivante :
a/b varie de 0 à 50,
a/d varie de 0 à 50,
b/d varie de 0,01 à 10 ,et
d/(a + b) varie entre 4:1 et 1:20, et
la somme de (a + b + d) est telle que le polymère phosphoné ait un poids moléculaire allant de 1000 à 20 000 000, et ledit procédé comportant la mise en réaction, à une température d'au moins 110 °C pendant au moins 1/4 heure, dans un solvant commun aqueux, de

(A) un polymère ayant la structure



dans laquelle R ,M, a et b ont la signification donnée plus haut et la somme de (a + b) est telle que le poids moléculaire du polymère soit d'au moins 2000, avec

(B) un réactif chimique ayant la structure

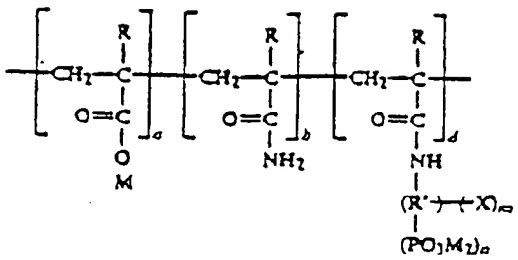


dans laquelle R_1, M et X sont définis plus haut et m va de 0 à 3, n varie de 1 à 3 et la somme de (m + n) varie de 1 à 4, et le rapport du réactif au polymère s'étend entre environ 1:1 et environ 1:10 et la pression de réaction est d'au moins 123 kPa,

et ensuite la récupération dudit polymère phosphoné.

7. Procédé selon la revendication 5 ou 6 dans lequel le solvant est l'eau ou une émulsion eau dans l'huile.

8. Procédé selon la revendication 1 ou 2 pour synthétiser un polymère phosphoné de formule V



dans laquelle

R' est un groupe alkylène linéaire ou ramifié de pontage ayant de 1 à 6 atomes de carbone,

X est choisi parmi -OH et -COOH et leurs mélanges,

R est choisi de façon individuelle à chaque fois à partir de l'hydrogène et des groupes méthyle et éthyle,

M est choisi de façon individuelle à chaque fois à partir de l'hydrogène, des groupes alkyles inférieurs en C_1-C_4,du sodium, du potassium, des amines tertiaires, des amines quaternaires et des ions ammonium et de leurs mélanges;

m va de 0 à 3,

n va de 1 à 3, et

la somme de (n + m) va de 1 à 4,

a, b et d sont des nombres entiers ayant les relations :

a/d va de 0 à 50,

a/b va de 0 à 50,

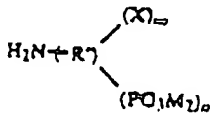
b/d va de 0,1 à 20,

d/(a + b) va de 5:1 à 1:10,

la somme de (a + b + d) est suffisante pour donner un poids moléculaire d'au moins 2000,

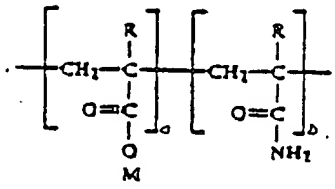
ledit procédé comportant la mise en réaction dans un solvant aqueux, pendant au moins 1/2 heure à une température d'au moins 110 ° C, dans un réacteur contrôlé en pression, des ingrédients

(A) un réactif chimique de formule



dans laquelle R', X, M, m et n ont la signification donnée plus haut, et

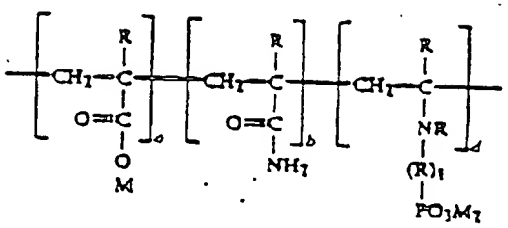
(B) un polymère vinylique soluble dans l'eau ayant des groupes amides pendants représenté par la formule



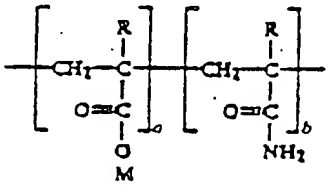
dans laquelle R, M, a et b ont la signification donnée plus haut, et de telle sorte que le rapport molaire du réactif aux groupes amides pendants sur le polymère s'étende entre environ 1:1 et environ 1:5,

ledit procédé comportant ensuite la récupération du polymère phosphoné.

9. Polymère phosphoné ayant la formule générale



et étant synthétisé, dans un réacteur contrôlé en pression, en faisant réagir un polymère précurseur ayant la formule



avec un réactif chimique

$H_2N\{R_1\}PO_3M_2$

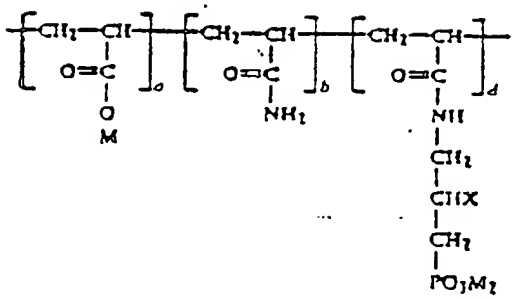
dans un solvant aqueux à une température d'au moins 100 °C pendant au moins 1/4 heure, avec un rapport molaire entre le polymère précurseur et le réactif chimique s'étendant entre environ 20:1 et environ 1:2, et où

- R_1 est un groupe de pontage alkylène inférieur linéaire ou ramifié contenant de 1 à 6 atomes de carbone,
- R est choisi de façon individuelle à chaque fois à partir des groupes hydrogène et méthyle,
- M est choisi de façon individuelle à chaque fois à partir de l'hydrogène, des groupes alkyles inférieurs en C_1-C_4, des ions des métaux alcalins, des amines tertiaires, des amines quaternaires et de l'ammonium ainsi que leurs mélanges,

a, b et d sont des nombres entiers ayant les relations :
a/d va de 0 à 100,
a/b va de 0 à 100,
b/d va de 0,01 à 100, et
d/(a + b) s'étend entre 10:1 et 1:100, et où la somme de (a + b + d) est telle que le polymère phosphoné ait un poids moléculaire d'au moins 1000.

10. Polymère phosphoné selon la revendication 9 qui est synthétisé dans un solvant de réaction aqueux à une température d'au moins 120 °C pendant au moins 1 heure avec un rapport molaire entre le polymère précurseur et le réactif chimique allant de 10:1 à 1:1 et où
R est l'hydrogène,
M est choisi parmi l'hydrogène, les ions sodium, potassium et ammonium et leurs mélanges,
et le polymère a un poids moléculaire entre 2000 et 20 000 000.

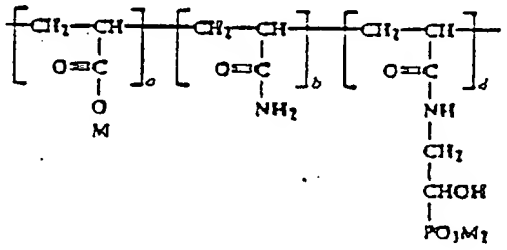
11. Polymère phosphoné représenté par la formule générale



dans laquelle

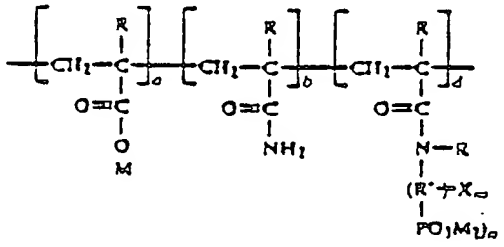
M	est choisi de façon individuelle à chaque fois parmi l'hydrogène, les ions sodium et ammonium,
X	est choisi parmi les groupes -OH, -COOH, $-(OCH_2CH_2)_p-OH$, $-SO_3H$ et leurs mélanges,
p	va de 1 à 6,
a, b et d	sont des nombres entiers tels que la somme de (a + b + d) est suffisante pour obtenir un poids moléculaire d'au moins 1000, a/d va de 0 à 100, b/d va de 0,01 à 100, a/b va de 0 à 100, et le rapport d/(a + b) s'étend entre 5:1 et 1:50.

12. Polymère phosphoné représenté par la formule générale



où M, a, b, d ont la signification définie dans la revendication 11.

13. Polymère phosphoné représenté par la formule générale



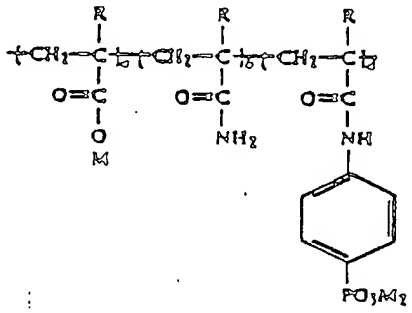
dans laquelle

R'	est un groupe hydrocarboné multivalent de pontage ayant de 1 à 6 atomes de carbone et étant choisi à partir des groupes alkyles linéaires, alkyles ramifiés, cycliques et oléfiniques et leurs mélanges;
X	est choisi parmi -OH et -COOM et leurs mélanges;
R	est choisi de façon individuelle à chaque fois à partir des groupes hydrogène et méthyle;

M est choisi de façon individuelle à chaque fois à partir de l'hydrogène, des groupes alkyles inférieurs en C_1-C_4, des ions sodium, potassium et ammonium et de leurs mélanges;

a, b et d sont des nombres entiers dont la somme est telle que le poids moléculaire du polymère phosphoné soit d'au moins 2000,
où il existe les relations suivantes :
a/b va de 0 à 100,
a/d va de 0 à 100,
b/d va de 0,01 à 100, et
le rapport d/(a+b) varie entre environ 10:1 et environ 1:100;
m va de 0 à 6,
n va de 1 à 6, et
la somme de (m+n) est comprise entre 1 et 6.

14. Polymère phosphoné représenté par la formule générale



où

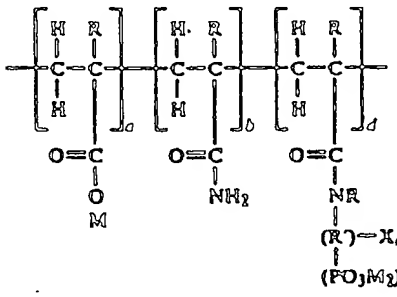
R est choisi de façon individuelle à chaque fois à partir des groupes hydrogène et méthyle;

M est choisi de façon individuelle à chaque fois à partir de l'hydrogène, un groupe méthyle, les ions sodium, potassium et ammonium, et de leurs mélanges, et

a, b et d sont les mêmes que dans la revendication 13.

Patentansprüche

1. Verfahren zur Synthetisierung von wasserlöslichen phosphonierten Polymeren mit statistisch wiederkehrenden Einheiten der allgemeinen Formel



(V)

worin

R' eine mehrwertige Kohlenwasserstoff-Brückengruppe mit 1 bis 16 Kohlenstoffatomen ist, ausgewählt aus linearen, verzweigtkettigen oder cyclischen Alkyl-, Alkaryl-, Arylalkyl-, aromatischen, heterozyklischen und olefinischen funktionellen Gruppen und Gemischen derselben,

X ausgewählt ist aus Cl, Br, J, -COOM, $-SO_3M$, -OH, -OR,

$$-(-OCH_2CH)_pOR$$
$$\quad\quad R$$

und Gemischen derselben,

R jeweils einzeln ausgewählt ist aus H und niederen C_1-C_4-Alkylgruppen,

M ausgewählt ist aus Wasserstoff, niederen C_1-C_4-Alkylgruppen, Alkalimetall, einem Äquivalent von Erdalkalimetallen, alkylierten und tertiären Aminen, quaternären Aminen und dem Ammoniumion sowie Gemischen derselben; und

a, b und d ganze Zahlen sind mit folgender Beziehung:
a/b läuft von Null bis 100,
b/d läuft von 0,01 bis 100,
a/d läuft von Null bis 100,
und die Summe von (a+b+d) reicht aus, um ein Molekulargewicht von mindestens 500 vorzugeben, und das Verhältnis von d/(a+b) reicht von 100:1 bis 1:100,

p liegt zwischen 1 und 16,

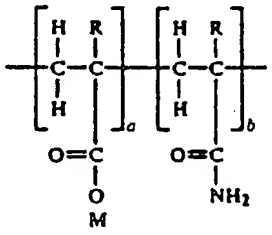
m liegt zwischen 0 und 16, und

n liegt zwischen 1 und 16,

mit der Maßgabe, daß, wenn M Null ist, dann die Summe aus (m+n) von 1 bis 20 reicht,

dadurch gekennzeichnet, daß in einem üblichen Lösungsmittel bei einer Temperatur von mindestens 100 °C umgesetzt werden

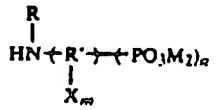
(A)ein Polymer mit einem Molekulargewicht von mindestens 500 und mit funktionellen Amid-Seitengruppen, entsprechend der Strukturformel



worin R, M, a und b die vorstehende Bedeutung haben,

mit

(B) einem chemischenReaktanten der Strukturformel



(I)

worin R, R', M, X, p, m und n die vorstehende Bedeutung haben,

wobei das Molverhältnis des chemischen Reaktanten zu Amid-Seitengruppen in dem Polymeren im Bereich zwischen etwa 5:1 und etwa 1:100 eingestellt und die Umsetzung bis zu einem Umsatz des chemischen Reaktanten zu phosphonierten Seitengruppen an dem Polymer von mindestens 25 Prozent ausgeführt wird und man anschließend das wasserlösliche phosphonierte Polymer gewinnt.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß

R' mindestens zwei Kohlenstoffatome aufweist und linear, cyclisch, aromatisch oder eine Mischung derselben ist,

X ausgewählt ist aus -OH, -COOH,

$$-(-OCH_2\underset{R}{\underset{|}{C}}H)_p-OR$$

und Gemischen derselben,

R jeweils einzeln ausgewählt ist aus Wasserstoff, Methyl- und Ethylgruppen,

M jeweils einzeln ausgewählt ist aus Wasserstoff, niederen C_1-C_4-Alkylgruppen, Natrium, Kalium, tertiären Aminen, quaternären Aminen, Ammonium und Gemischen derselben,

p von 1 bis 12 reicht,

m von 0 bis 4 reicht,

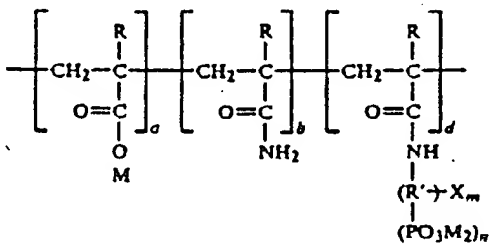
n von 1 bis 4 reicht,

und das Molekulargewicht des wasserlöslichen phosphonierten Polymers im Bereich zwischen etwa 2.000 und etwa 20.000.000 liegt.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das übliche Lösungsmittel aus der folgenden Gruppe ausgewählt ist: Wasser, Dimethylformamid, Dimethylsulfoxid, Diethylenglykoldimethylether und Gemische derselben.

4. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß das Lösungsmittel aus der folgenden Gruppe ausgewählt ist: Wasser und in einer kontinuierlichen Ölphase emulgiertes Wasser, so daß das wasserlösliche phosphonierte Polymer entweder als Wasser-in-Öl-Emulsion oder als wäßrige Lösung gewonnen wird.

5. Verfahren nach einem der Ansprüche 1 bis 4 zur Synthetisierung von wasserlöslichen phosphonierten Polymeren der Formel V



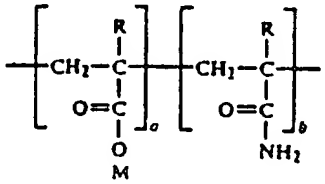
dadurch gekennzeichnet, daß

R Wasserstoff und

R' ausgewählt ist aus mehrwertigen verzweigtkettigen Alkyl-, linearen Alkyl- oder cyclischen Kohlenwasserstoff-Brückengruppen mit 1 bis 8 Kohlenstoffatomen,

wobei in einem wäßrigen Lösungsmittel umgesetzt werden

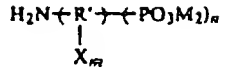
(A) ein Polymer mit funktionellen Amid-Seitengruppen der Strukturformel



worin R, M, a und b die vorstehende Bedeutung haben und die Summe von (a + b) ein Molekulargewicht von mindestens 500 erreicht,

mit

(B) einem Reaktanten der Strukturformel



worin R', M, X, m und n die vorstehende Bedeutung haben, unten den folgenden Reaktionsbedingungen:

(I) Reaktionstemperatur von mindestens 100 °C,

(II) Reaktionszeit von mindestens 1/4 Stunde,

(III) Molverhältnis von chemischem Reaktanten zu Polymer im Bereich zwischen etwa 2:1 und etwa 1:50,

(IV) Druck im Bereich von Atmosphärendruck bis zum 35fachen Atmosphärendruck,

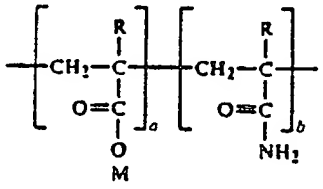
wodurch diese phosphonierten Polymeren erhalten und anschließend gewonnen werden.

6. Verfahren nach Anspruch 5, dadurch gekennzeichnet, daß

R'	eine lineare Alkylen-Brückengruppe mit 2 bis 6 Kohlenstoffatomen ist;
X	ausgewählt ist aus -OH, -COOH, $-(-OCH_2CH_2)_p-OH$ und Gemischen derselben;
R	jeweils einzeln ausgewählt ist aus Wasserstoff und Methyl;
M	jeweils einzeln ausgewählt ist aus Wasserstoff, niederen C_{1-4}-Alkylgruppen, Natrium, Kalium, Ammonium und Gemischen derselben;
a, b und d	ganze Zahlen sind mit der folgenden Beziehung: a/b läuft von 0 bis 50, a/d läuft von 0 bis 50, b/d läuft von 0,01 bis 10, und d/(a + b) liegt im Bereich zwischen 4:1 und 1:20, und die Summe von (a + b + d) ist derart, daß das phosphonierte Polymer ein Molekulargewicht im Bereich von 1.000 bis 20.000.000 aufweist,

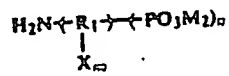
wobei die Umsetzung bei einer Temperatur von mindestens 110 °C für mindestens 1/4 Stunde in einem üblichen wäßrigen Lösungsmittel erfolgt zwischen

(A) einem Polymer der Strukturformel



worin R, M, a und b die vorstehende Bedeutung haben und die Summe von (a + b) derart ist, daß das Molekulargewicht des Polymeren mindestens 2.000 erreicht, und

(B) einem chemischen Reaktanten der Strukturformel



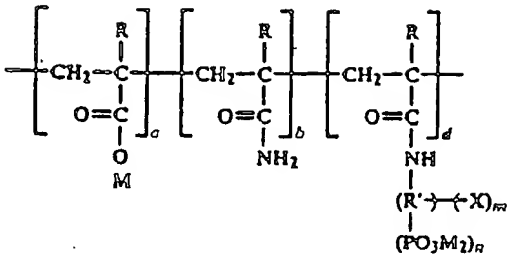
worin R_1, M und X wie vorstehend definiert sind und m von 0 bis 3, n von 1 bis 3 und die Summe von (m + n) von 1 bis 4 reicht,

wobei das Verhältnis von Reaktant zu Polymer im Bereich zwischen etwa 1:1 bis etwa 1:10 und der Reaktionsdruck mindestens 123 kPa beträgt, und

anschließend dieses phosphonierte Polymer gewonnen wird.

7. Verfahren nach Anspruch 5 oder 6, dadurch gekennzeichnet, daß das Lösungsmittel Wasser oder eine Wasser-in-Öl-Emulsion ist.

8. Verfahren nach Anspruch 1 oder 2 zur Synthetisierung eines phosphonierten Polymeren der Formel V

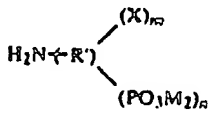


worin

R'	eine lineare oder verzweigtkettige Alkylen-Brückengruppe mit 1 bis 6 Kohlenstoffatomen ist,
X	ausgewählt ist aus -OH und -COOH und Gemischen derselben,
R	jeweils einzeln ausgewählt ist aus Wasserstoff-, Methyl- und Ethylgruppen,
M	jeweils einzeln ausgewählt ist aus Wasserstoff, niederen C_1-C_4-Alkylgruppen, Natrium, Kalium, tertiären Aminen, quaternären Aminen und Ammoniumionen und Gemischen derselben,
m	von 0 bis 3 läuft,
n	von 1 bis 3 läuft, und
	die Summe von (m + n) von 1 bis 4 reicht,
a, b und d	ganze Zahlen sind mit folgender Beziehung:
	a/d läuft von 0 bis 50,
	a/b läuft von 0 bis 50,
	b/d läuft von 0,1 bis 20,
	d/(a + b) läuft von 5:1 bis 1:10,
	die Summe von (a + b + d) ist derart, daß ein Molekulargewicht von mindestens 2.000 vorgegeben wird,

wobei in einem wäßrigen Lösungsmittel für mindestens 1/2 Stunde bei einer Temperatur von mindestens 110 °C in einem druckgesteuerten Reaktor die folgenden Bestandteile umgesetzt werden:

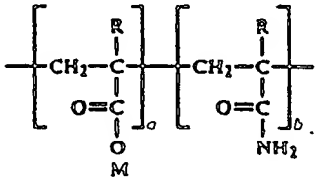
(A) ein chemischer Reaktant der Formel



worin R', X, M, m und n die vorstehende Bedeutung haben,

und

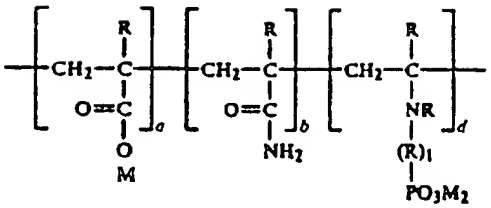
(B) ein wasserlösliches Vinylpolymer mit Amidseitengruppen der Formel



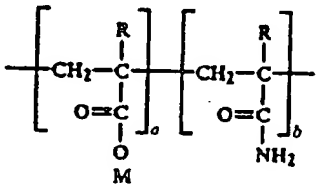
worin R, M, a und b die vorstehende Bedeutung haben,

wobei das Molverhältnis von Reaktant zu Amidseitengruppen an dem Polymer im Bereich zwischen etwa 1:1 und etwa 1:5 eingestellt wird und anschließend das phosphonierte Polymer gewonnen wird.

9. Phosphoniertes Polymer der allgemeinen Formel



synthetisiert in einem druckgesteuerten Reaktor durch Umsetzen eines Vorläuferpolymers der Formel



mit einem chemischen Reaktanten

$H_2N\{R_1\}PO_3M_2$

in einem wäßrigen Lösungsmittel bei einer Temperatur von mindestens 100 °C für mindestens 1/4 Stunde bei einem Molverhältnis von Vorläuferpolymer zu chemischem Reaktant im Bereich zwischen etwa 20:1 bis etwa 1:2, worin

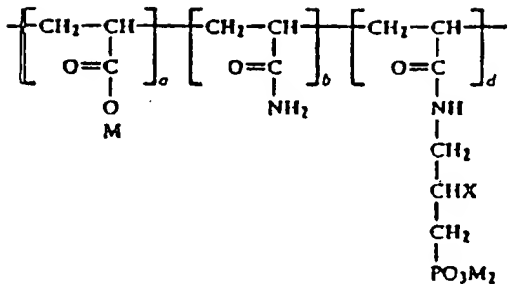
- R_1 eine lineare oder verzweigtkettige niedere Alkylen-Brückengruppe mit 1 bis 6 Kohlenstoffatomen ist,
- R jeweils einzeln ausgewählt ist aus Wasserstoff- und Methylgruppen,
- M jeweils einzeln ausgewählt ist aus Wasserstoff, niederen C_1-C_4-Alkylgruppen, Alkalimetall, tertiären Aminen, quaternären Aminen und Ammoniumionen und Gemischen derselben,
- a, b und d ganze Zahlen sind mit folgender Beziehung:
  a/d läuft von 0 bis 100,
  a/b läuft von 0 bis 100,
  b/d läuft von 0,01 bis 100, und
  d/(a+b) liegt im Bereich zwischen 10:1 und 1:100, wobei die Summe von (a+b+d) derart ist, daß das phosphonierte Polymer ein Molekulargewicht von mindestens 1.000 aufweist.

10. Phosphoniertes Polymer nach Anspruch 9, synthetisiert in einem wäßrigen Reaktionslösungsmittel bei einer Temperatur von mindestens 120 °C für mindestens 1 Stunde bei einem Molverhältnis von Vorläuferpolymer zu chemischem Reaktant von 10:1 bis 1:1, wobei

- R Wasserstoff ist,
- M ausgewählt ist aus Wasserstoff, Natrium, Kalium und Ammoniumionen und Gemischen derselben,

und das Polymer ein Molekulargewicht zwischen 2.000 und 20.000.000 aufweist.

11. Phosphoniertes Polymer der allgemeinen Formel



worin

M jeweils einzeln ausgewählt ist aus Wasserstoff, Natrium- und Ammoniumionen,

X ausgewählt ist aus den Gruppen -OH, -COOH, $-(OCH_2CH_2)_p-OH$, $-SO_3H$ und Gemischen derselben,

p von 1 bis 6 läuft,

a, b und d ganze Zahlen derart sind, daß die Summe von (a + b + d) ausreicht, um ein Molekulargewicht von mindestens 1.000 zu erreichen,

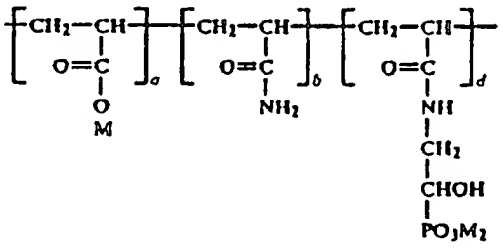
a/d von 0 bis 100,

b/d von 0,01 bis 100,

a/b von 0 bis 100 läuft und

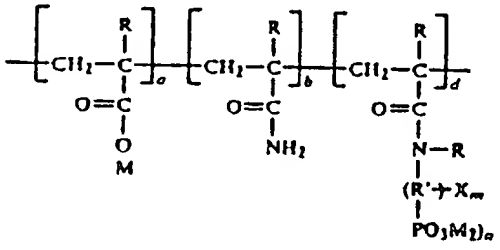
das Verhältnis d/(a + b) im Bereich zwischen 5:1 und 1:50 liegt.

12. Phosphoniertes Polymer der allgemeinen Formel



worin M, a, b und d die vorstehend in Anspruch 11 definierte Bedeutung haben.

13. Phosphoniertes Polymer der allgemeinen Formel



worin

R' eine mehrwertige Kohlenwasserstoff-Brückengruppe mit 1 bis 6 Kohlenstoffatomen und ausgewählt ist aus linearen Alkyl-, verzweigtkettigen Alkyl-, cyclischen und olefinischen Gruppen und Gemischen derselben,

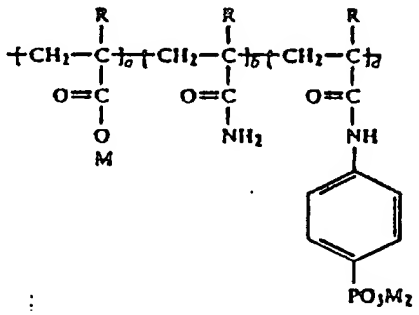
X ausgewählt ist aus -OH, -COOM und Gemischen derselben,

R jeweils einzeln ausgewählt ist aus Wasserstoff und Methylgruppen,

M jeweils einzeln ausgewählt ist aus Wasserstoff, niederen C_1-C_4-Alkylgruppen, Natrium, Kalium und

Ammoniumionen und Gemischen derselben,
a, b und d ganze Zahlen sind, deren Summe derart ist, daß das Molekulargewicht des phosphonierten Polymers mindestens 2.000 ist,
wobei die folgende Beziehung gilt:
a/b läuft von 0 bis 100,
a/d läuft von 0 bis 100,
b/d läuft von 0,01 bis 100, und
das Verhältnis d/(a + b) liegt zwischen etwa 10:1 bis etwa 1:100,
m gleich 0 bis 6 ist,
n gleich 1 bis 6 ist, und
die Summe von (m + n) zwischen 1 und 6 liegt.

14. Phosphoniertes Polymer der allgemeinen Formel



worin

R	jeweils einzeln ausgewählt ist aus Wasserstoff und Methylgruppen,
M	jeweils einzeln ausgewählt ist aus Wasserstoff, Methyl, Natrium, Kalium und Ammoniumionen und Gemischen derselben, und
a, b und d	die gleiche Bedeutung haben wie in Anspruch 13.